

PATENT SPECIFICATION

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Graft copolymers and shaped articles consisting of or containing them.

COMPLETE SPECIFICATION

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of
5 Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention concerns new graft copolymers of acrylic or methacrylic acid and polyolefins and pertains to a method of making the same. It relates more particularly to graft copolymers consisting of a predominant amount of polyethylene or polypropylene having a minor proportion of polymer chains of acrylic or methacrylic acid chemically combined to the polyolefin substrate.

In general, polymerized olefins such as polyethylene and polypropylene are tough-semi-transparent thermoplastic materials having good resistance to many chemicals and can be molded by usual injection molding or extrusion operations to form articles suitable for a variety of purposes in the home and industry. The polymers can be fabricated into sheet or film having a high degree of moisture impermeability and are heat sealable. Because of this combination of properties films of the polymers are highly useful for packaging and wrapping a great variety of materials, such as chemicals, fresh produce, dried milk, textiles, hardware, etc., and are useful for coating other materials such as paper, cloth or metal, e.g. aluminium foil.

However, a disadvantage of the polymers of ethylene and propylene as film or sheet for use in the packaging field is the fact that standard aniline and rotogravure printing inks, employed for printing various cellulosic films, do not adhere satisfactorily to the surface of the film. Another disadvantage

of the polymers is that they are not readily receptive of dyes and do not readily adhere to many materials, particularly when applied as a thin film to metal or metal foil.

The novel graft copolymers of the present invention and the articles shaped therefrom do not have these disadvantages. The graft copolymers of the invention generally comprise from 98 to 75 percent of a polymerized monoolefin containing from 2 to 3 carbon atoms in the molecule and grafted thereon from 2 to 25 percent by weight of polymer chains of a monoethylenically unsaturated carboxylic acid such as acrylic acid and/or methacrylic acid. The polymerized monoolefin of backbone material may be polyethylene, polypropylene, or a copolymer of ethylene and propylene.

If the novel graft copolymers are used in shaped articles, it is important that the composition of the graft copolymer is kept within the above stated ranges in order to produce articles and structures having optimum physical properties in combination with the desirable improvements offered by the present invention. Among the desirable properties are good receptivity for dyes and printing inks and excellent adherence to metals, particularly to metal foils. The graft copolymers can readily be fabricated into shaped articles by usual injection or extrusion operations or by calendering procedures without destroying or impairing the excellent levels of physical properties.

The new graft copolymers can readily be prepared by reacting acrylic acid or methacrylic acid with a normally solid homopolymer of an olefin such as ethylene or propylene or a copolymer of ethylene and propylene or a mixture of polyethylene and polypropylene to form a graft copolymer containing from 2 to 25 percent by weight of polymer chains of the acrylic acid or methacrylic acid chemically combined, i.e. grafted-onto, correspondingly from 98 to

75 per cent by weight of the polyolefin polymer.

Thus the preferred process for the production of the graft copolymers of the invention comprises creating active centres or sites, which are capable of initiating vinyl polymerization, along the chains of a polymer or copolymer of ethylene and/or propylene. The activated polymer is then reacted with acrylic or methacrylic acid, preferably at a temperature between 65° and 175°C. Among the various methods available to produce the active centres or sites on the preformed polyolefin, it is preferred to subject the polyolefin to high energy ionizing radiation. Generally, it is desirable that the high energy ionizing radiation has an intensity of at least 40,000 rads per hour. Acrylic or methacrylic acid can readily be grafted, in the above stated proportion, on to the polyolefin backbone material if the polyolefin is subjected to radiation for a total dose of from 0.5 to 10 megarads. Though the grafting reaction can be carried out in the absence of solvents it is generally preferred that an organic solvent for the polymer, or graft copolymer respectively, is present during the grafting reaction.

The polyolefin starting material can be polyethylene, polypropylene, mixtures of polyethylene and polypropylene or copolymers of ethylene and propylene. The polymer starting material is preferably one having a melt index between about 0.1 and 60 and can be in powder, granular or shaped form such as sheet, film, rod, bars, filaments, fibers or other molded configuration, but is preferably employed in powder or granular form.

The graft copolymers are prepared by reacting acrylic acid or methacrylic acid with the solid polyolefin having active centres on the polymer molecules capable of initiating the polymerization of vinyl or vinylidene monomers to form addition polymers. Active centres at which grafting will occur can readily be induced on the polyolefin in known ways, e.g. by subjecting the solid polyolefin to the action of high energy ionizing radiations such as gamma rays, X-rays or high speed electrons, preferably in the presence of air or oxygen for a dose of from 0.5 to 10 megarads in a field of high energy ionizing radiations of an intensity of at least 40,000 rads per hour or the equivalent thereof.

The radiation doses can be expressed in units of megarads. The "rad" expressing the quantity of radiations of particles of high energy giving place to an energy absorption of 100 ergs of energy per gram of water of equivalent absorbing material. The doses can also be expressed in terms of the exposure to radiation, in watt-seconds per gram of the material such as is produced by using

a Van de Graaff electron accelerator operating at, for example, a current in the tube of 250 microamperes and an acceleration potential of 2 million electron volts (Mev).

Alternatively, active sites on the polyolefin at which grafting of the acrylic acid or methacrylic acid will occur can be produced by contacting the solid polymer with ozone, suitably in a gaseous or liquid medium, e.g. air, oxygen or carbon tetrachloride, which is a non-solvent for the polymer, for a period of a few seconds to several hours depending upon the temperature, whereby active ozonide sites are produced on the polyolefin. The polyolefin is advantageously contacted with a gaseous atmosphere such as air or oxygen containing from 1 to 10 per cent by volume of ozone at temperatures between about -20° and 160°C. Reaction of the ozone with the polyolefin occurs more readily as the temperature is increased.

The number of the active centres induced on the polyolefin starting material is dependent in part upon the intensity and dose of irradiation or upon the concentration of the ozone and in part upon the temperature at which the activating of the polyolefin is carried out.

The number and the length of the polymer chains of acrylic or methacrylic acid chemically attached to the trunk polyolefin polymer is in turn dependent upon a number of variables among which are the number of active centres on the polymer starting material, the concentration of the grafting monomer and the temperature at which the grafting reaction is carried out.

The grafting reaction can be carried out by contacting the polyolefin containing active centres with the acrylic or methacrylic acid in vapour or liquid form and in the presence or absence of a diluent which may swell or dissolve the polyolefin. The graft copolymers are preferably prepared by reacting the polyolefin, containing active centres, with the liquid monomers, or in a mixture of monomers and a liquid solvent for the monomers which can swell, or dissolve the polymer.

It is important in carrying out the grafting reaction that the polyolefin containing the active centres be contacted with the grafting monomeric acrylic or methacrylic acid in a non-dissolved form, i.e. as swelled or non-swelled particles, until the grafting reaction is initiated, in order to avoid destroying the active sites on the polymer. After initiating the grafting reaction the mixture of the polyolefin, the monomer and/or a solvent can be heated at reaction temperatures such that the polymer is dissolved while continuing the grafting reaction. In other words the polyolefin containing active sites should not be

dissolved in a solvent prior to contacting it with the acrylic acid or methacrylic acid and initiating the grafting reaction.

The grafting reaction can be carried out at temperatures between 65° and 170°C. and at atmospheric, subatmospheric or superatmospheric pressure. The reaction is preferably carried out at temperatures below the crystalline melting point of the polyolefin and in the absence or substantial absence of air or oxygen.

Suitable liquid diluents for carrying out the reaction of the acrylic acid or methacrylic acid with the activated polyolefin are benzene, toluene, xylene, dioxane, hexane, heptane, and octane. The reaction is advantageously carried out in a liquid medium employing the acrylic or methacrylic acid and diluent in amount sufficient to form a slurry or mixture with the polyolefin that can conveniently be stirred, and employing the acid in a concentration of from 10 to 50 per cent by weight of the sum of the weights of the acid and the diluent initially used.

In practice, the polyethylene or polypropylene having active centers along the polymer chains such as those induced by high energy ionizing radiations, and preferably in the form of small particles, is suspended in a liquid body of acrylic acid or methacrylic acid, with or without a diluent such as toluene, in a suitable reaction vessel. The mixture is stirred and heated at a reaction temperature between 65° and 170°C. for a time sufficient to react the acrylic or methacrylic acid with the activated polyolefin and form a graft copolymer containing from 2 to 25 per cent by weight of said acid chemically combined as polymer chains attached to from 98 to 75 per cent by weight of the polyolefin.

Upon completing the reaction the polymer is recovered and is washed with a suitable liquid, e.g. water or an organic solvent, to remove and separate homopolymer of the acrylic or methacrylic acid formed in the reaction to produce the graft copolymer. The graft copolymer is thereafter dried, suitably by heating the same in an oven at temperatures between 60° and 110°C. and under reduced pressure.

The graft copolymers of the invention are thermoplastic resinous products consisting of from 2 to 25 per cent by weight of polymer chains of acrylic acid or methacrylic acid chemically attached to from 98 to 75 per cent of polyethylene or polypropylene. The graft copolymers can be moulded by usual compression and injection moulding operations or by extrusion methods to form

articles useful for a variety of purposes. The product can be moulded to form boxes, cups, or other containers or it can be extruded into rod, sheet or fiber or calendered into sheet or film and applied to other substrate material such as cloth, paper or metal sheet or foil such as zinc, copper, brass or aluminium.

The carboxylic acid group of the graft copolymers can be converted to salt groups such as the sodium, calcium, barium, magnesium or copper salts which confers on the polymer unexpected properties such as increased heat resistance, antistatic properties or hydrophilic characteristics or to increase their receptivity for printing inks or dyes.

The following examples illustrate ways in which the principle of the invention has been applied, but are not to be construed as limiting its scope.

EXAMPLE 1

High pressure polyethylene having a melt index of 19.2 and in the form of particles of sizes between 10 and 50 mesh per inch as determined by U.S. Standard screens was irradiated in air with high speed electrons from a Van de Graaff generator operating at a beam current of 156 microamperes and 2 Mev potential for a total dose of 4 megarads. In each of a series of experiments, a charge of 175 grams of the irradiated polyethylene was suspended in a solution of 1000 ml. of dioxane containing acrylic acid in amount as stated in the following table. The graft polymerization was carried out in a glass reaction vessel equipped with a reflux condenser and stirrer and under a blanket of pre-purified nitrogen gas by heating the mixture at a temperature of 70°C. for a time as stated in the table. After completing the reaction the product was separated by filtering and was washed with dioxane to remove homopolymer and unreacted acrylic acid, then was washed with acetone and dried in an oven at 60°-70°C. and 10 millimeters absolute pressure to a constant weight. Table I identifies the experiments and gives the weight in grams of the irradiated polyethylene and acrylic acid initially used. The table gives the polymerization conditions and the per cent of acrylic acid in the graft copolymer product. The per cent of graft is determined by the equation:

$$\text{Per Cent Graft} = \frac{P - P_0}{P} \times 100$$

wherein P_0 is the weight of the irradiated polyethylene initially used and P is the weight of the graft copolymer product.

TABLE I

5	Run No.	Starting Materials		Temp. °C.	Polymerizing Conditions		Product	
		Polyethylene gm.	Acrylic Acid gm.		Time Hrs.	Weight gms.	Acrylic Acid Graft %	
	1	175	106.5	70	7.0	178.6	2.05	
	2	175	185.5	70	6.3	191.1	9.2	
	3	175	268.0	70	5.0	208.8	19.3	

10 EXAMPLE 2

High pressure polyethylene in the form of moulding powder and having a melt index of 20 was irradiated in air with high speed electrons from a Van de Graaff generator operating at a beam current of 110 microamperes and 2 Mev potential to a total dose of 2.8 megarads. A charge of 300 grams of the irradiated polyethylene was placed in a glass-reaction vessel equipped with a reflux condenser and stirrer, together with 2150 ml. of toluene. The mixture was stirred and 300 ml. of acrylic acid, containing 200 parts of dimethyl ether of hydroquinone per million parts of the acrylic acid as polymerization inhibitor, was added. The resulting mixture was stirred and heated at temperatures between 91° and 92° for 68 minutes. The reaction was carried out under an atmosphere of pre-purified nitrogen gas. After the mixture had cooled to 70°C. a charge of 750 ml. of methyl alcohol was added with stirring. The product was separated by filtering. It was slurried in 1975 ml. of methyl alcohol and was again separated by filtering. The filter cake was suspended in 2900 ml. of 0.5 normal aqueous sodium hydroxide solution and was heated at temperatures between 60° and 90°C. for one hour, then was separated by filtering and was washed with water. It was reslurried in 2400 ml. of 0.5 normal aqueous hydrochloric acid solution and was filtered. The product was washed with water, then with acetone and was dried in a vacuum oven at 60°-70°C. and 10 millimeters absolute pressure. There was obtained 344 grams of graft copolymer product containing 10.4 per cent by weight of acrylic acid graft copolymerized onto the polyethylene initially used.

EXAMPLE 3

High pressure polyethylene having a melt index of 2.1 and in the form of a finely ground powder was irradiated in air with high speed electrons from a Van de Graaff generator operating at a beam current of 220 microamperes and 2 mev potential to a dose of 4 megarads. In each of a series of experiments a charge of the irradiated polyethylene was reacted with acrylic acid employing procedures similar to those described in the preceding examples to form a graft copolymer containing acrylic

acid chemically combined in the copolymer molecule in amount as stated in the following table. Portions of the graft copolymer were injection moulded to form test pieces of 1/8 x 1/2 inch cross section by 4 inches long. These test pieces were employed to determine the modulus of elasticity for the graft copolymer employing procedure similar to that described in ASTM D790-49T.

Other moulded test pieces were used to determine a hydrophilic characteristic for the product. The procedure for determining the hydrophilic characteristic was to weigh a test bar then immerse the bar in boiling water for a period of 15 minutes. It was then removed from the water and was blotted dry with cleansing tissue and allowed to stand in air at room temperature for one hour, then was re-weighed. The increase in weight is a measure of the hydrophilic characteristic of the graft copolymer to absorb water.

Other portions of the graft copolymer were compression moulded onto a brass sheet 1/8 inch thick at temperatures between 185° and 200°C. under an applied pressure of 8000 pounds per square inch gauge pressure to form a graft copolymer film adhered to the brass sheet. The adhered film was cut into test sections 1-inch wide. An end of a test section was separated from the brass sheet. The end of the film was secured in a movable clamp. The load in grams required to strip the adhered test section of the film from the brass sheet was determined. The load required to strip the adhered test portion of the film from the brass sheet was determined within 2 hours after they were prepared and after ageing the prepared film in air at room temperature for 6 days. Table II identifies the experiments and gives the per cent by weight of acrylic acid grafted onto the polyethylene. The table also gives the modulus of elasticity determined for the copolymer, a hydrophilic characteristic for the product expressed as the per cent of gain in weight after immersion in boiling water as described above, and the load in grams required to strip a test section of the adhered graft copolymer film from the brass sheet. For purpose of comparison a test piece of the irradiated polyethylene was tested in similar manner.

TABLE II

5	Run No.	Graft Copolymer Acrylic Acid %	Modulus of Elasticity psi x 10 ⁻⁴	Hydrophilic Characteristic Water Absorbed %	Load to Strip graft copolymer film from brass sheet	
					As Prepared gms	Aged 6 days gms
10	1	0	1.6	0.06	380	570
	2	4.9	1.9	0.26	590	1330
	3	8.4	2.1	0.35	—	1470
	4	12.2	2.5	0.47	840	1690
	5	15.4	2.9	0.61	990	3200*
	6	21.0	3.4	0.93	990	2190*

* Graft copolymer film tears

15 Similar results of excellent adhesion of the graft copolymers to copper, magnesium, aluminium and steel sheets were obtained in other tests of the graft copolymers to metals.

20 All of the graft copolymers had excellent receptivity to basic dyes such as Brilliant Green B, Thioflavine TCND, Rhoduline Blue 6GA, Rhodamine B, Calcosyn brilliant Scarlet BN, and Eastman Fast Blue acetate dye.

25 EXAMPLE 4

Linear polyethylene having a melt index of 1.5 and in the form of a fine powder was subjected to a stream of oxygen containing 4 per cent by volume of ozone at room temperature and atmospheric pressure for a period of 5 minutes. A charge of 68 grams of the ozonized polyethylene, together with 400 ml. of an aqueous 8 per cent solution of acrylic acid, was placed in a glass ampoule which was purged with nitrogen gas and sealed. The materials were heated in the sealed ampoule at a temperature of 130°C. for a period of one hour, then were cooled and the product separated by filtering. The product was washed with hot water and was dried, there was obtained 72 grams of product containing 8.9 per cent by weight of acrylic acid graft copolymerized onto the polyethylene.

EXAMPLE 5

Two 150 gram samples of linear polyethylene powder of 1.1 melt index were

irradiated in air with high speed electrons from a Van de Graaff generator operating at a beam current and 2 mev potential for a time as stated in the table to a dose of 2 megarads. The irradiated polyethylene was suspended in 1075 ml. of toluene containing 150 ml. of acrylic acid. The mixture was stirred and heated at 70°C. for one hour. Thereafter, 1400 ml. of methyl alcohol was added. The resulting mixture was stirred for 10 minutes and was filtered to separate the product. The product was suspended in 2400 ml. of water and sodium hydroxide added in amount sufficient to bring the aqueous mixture to a pH of 10. The mixture was heated with stirring at temperatures between 70° and 90°C. for one hour, then was cooled and filtered. The product was suspended in 1520 ml. of water and the mixture made acidic to a pH between 2 and 3 with 12 normal aqueous hydrochloric acid solution. The mixture was filtered and the product was washed with 800 ml. of water, then with 800 ml. of acetone and was dried in a vacuum oven at temperatures between 60° and 70°C. and under 10 millimeters absolute pressure. Table III identifies the experiments and gives the beam current in microamperes at which the Van de Graaff generator was operated while irradiating the polyethylene. The table also gives the weight in grams of the graft copolymer product and the per cent of acrylic acid graft copolymerized onto the irradiated polyethylene.

TABLE III

85	Run No.	Beam Current Micro Amperes	Radiation Time Min.	Dose Megarads	Weight Grams	Acrylic Acid Graft %
	1	220	0.76	2	174	13.8
	2	5.5	30.3	2	173	13.3

90 EXAMPLE 6

High pressure polyethylene powder of 2.1 melt index was irradiated in air with high speed electrons from a Van de Graaff generator operating at a beam current of 220 microamperes and 2 mev potential to a dose of 3.2 megarads. In each of a series

of experiments, a charge of 300 grams of the irradiated polyethylene was suspended in about 2,000 ml. of toluene containing methacrylic acid in amount as stated in the following table. Pre-purified nitrogen gas was bubbled through the mixture while heating it at a temperature of 70°C. for a

reaction time as stated in the table. Thereafter, 500 ml. of methyl alcohol was added. The resulting mixture was allowed to cool and was filtered. The filter cake was slurried in 1950 ml. of methyl alcohol and filtered. The product was suspended in 3400 ml. of 0.2 normal aqueous sodium hydroxide solution and was heated at temperatures between 70° and 90°C. for one hour. It was filtered and the cake was washed with 600 ml. of water. The cake was slurried in 2550 ml. of 0.1 normal aqueous hydrochloric acid solution, then was filtered, washed with water, then with acetone and dried in a vacuum oven at 60°-70°C. and 10 millimeters absolute pressure. Table IV identifies the experiments and gives the ml. of methacrylic acid employed in making the graft copolymer and the reaction time in hours. The table also gives the weight in grams of the copolymer product and the per cent of methacrylic acid graft copolymerized onto the polyethylene.

TABLE IV

Run No.	Methacrylic Acid		Reaction Time		Product	
	Ml.		Hrs.		Weight Grams	Graft %
1	150		2		318	5.7
2	325		2		356	15.7
3	400		2.45		400	25.0

EXAMPLE 7

High pressure polyethylene powder of 2.1 melt index was irradiated with high speed electrons to a dose of 1.2 megarads employing procedure as described in Example 9. A charge of 150 grams of the irradiated polyethylene, together with 1,000 ml. of toluene and 150 ml. of methacrylic acid was placed in a reaction vessel. The mixture was stirred and heated at 70-72°C. for a period of 4 hours. The polymer was recovered employing procedure similar to that employed in Example 9. There was obtained 184 grams of copolymer product containing 18.4 per cent by weight of methacrylic acid graft copolymerized onto the polyethylene.

EXAMPLE 8

Moulding grade polypropylene in the form of a fine powder was irradiated in air with high speed electrons from a Van de Graaff generator operating at a beam current of 137 microamperes and 2 mev potential for a dose of 3.2 megarads. A charge of 100 grams of the irradiated polypropylene together with 1075 ml. of toluene and 100 ml. of acrylic acid was placed in a glass reaction flask equipped with a reflux condenser and stirrer. The mixture was stirred and heated at a temperature of 79°C. for one hour while purging the reaction vessel with nitrogen gas. Thereafter, 250 ml. of methyl alcohol was added. The product was separated by filtering. It was reslurried in 1000 ml. of methyl alcohol, stirred for 15 minutes and again filtered. The

filter cake was slurried a second time in 1,000 ml. of methyl alcohol, stirred for 20 minutes then filtered. The product was dried in a vacuum oven at 60°C. under 10 millimeters absolute pressure. There was obtained 108 grams of graft copolymer product containing 7.4 per cent by weight of acrylic acid chemically combined with the polypropylene polymer.

A portion of the graft copolymer was compression moulded at 185°C. on to aluminium foil 5 mils thick to form a composite sheet. The graft copolymer had good adhesion to the aluminium metal whereas polypropylene flash moulded on the aluminium foil did not adhere to the metal.

The graft copolymer when placed in a boiling one per cent aqueous solution of Rhodamine B dye took on a bright color that could not be removed by washing with hot water, methyl alcohol or acetone. Polypropylene was not colored by the dye.

EXAMPLE 9

A charge of .50 grams of a batch of powdered polypropylene was irradiated to a dose of 2 megarads with high speed electrons at a beam current of 175 microamperes and 2 mev potential. The irradiated polypropylene was placed in a glass reaction vessel, together with 700 ml. of toluene and 50 ml. of methacrylic acid. The mixture was heated at a temperature of 80°C. for one hour under an atmosphere of nitrogen gas, then was mixed with 1,000 ml. of methyl alcohol. The product was separated by filtering. The filter cake was reslurried in 1,000 ml. of methyl alcohol, was stirred for about 15 minutes and was filtered. This operation was repeated twice more, after which the product was dried in a vacuum oven at 50°C. and 10 millimeters absolute pressure. There was obtained 55.25 grams of graft copolymer product. It contained 9.5 per cent by weight of methacrylic acid graft copolymerized onto the polypropylene. A portion of the product was compression moulded at 185°C. and 8,000 p.s.i. pressure. The moulding was immersed in a one per cent aqueous Rhodamine B dye solution for one minute at 96°C. It was dyed a bright uniform colour. A moulded sheet of the polypropylene was not coloured when treated with the dye solution under similar conditions.

WHAT WE CLAIM IS:

1. Graft copolymer comprising 98 to 75 percent of a polymerized monoolefin containing from 2 to 3 carbon atoms in the molecule and grafted thereon from 2 to 25 percent by weight polymer chains of a monoethylenically unsaturated carboxylic acid, such as acrylic acid and/or methacrylic acid.

2. Graft copolymer in accordance with Claim 1 wherein the polymerized mono-

olefin is polyethylene.

3. Shaped articles, such as films or other structures having one dimension much smaller than the other two, which consist of or contain a graft copolymer comprising 98 to 75 percent of a polymerized monolefin containing from 2 to 3 carbon atoms in the molecule and grafted thereon, from 2 to 25 percent by weight polymer chains of a monoethylenically unsaturated carboxylic acid, such as acrylic acid and/or methacrylic acid.
4. Shaped articles in accordance with Claim 3 wherein the polymerized monolefin is polyethylene and the monoethylenically unsaturated carboxylic acid is acrylic acid.
5. Shaped article in accordance with Claims 3 or 4, characterized in that it has the shape of a film or thin sheet, one side of which is adhered or bonded to sheet metal and particularly foil.
6. Process for producing the graft copolymer of Claims 1 to 2, characterized in that one creates active centers or sites, which are capable of initiating vinyl polymerization, along the chains of a polymer or copolymer of ethylene and/or propylene and reacts the activated polymer with acrylic and/or methacrylic acid at a temperature

between 65 and 175°C.

7. Process in accordance with Claim 6, characterized in that one reacts 2 to 25 parts of unsaturated carboxylic acid with from 98 to 75 parts by weight of the polymer such that the reactants produce 100 parts by weight of the graft copolymer.

8. Process in accordance with Claim 6 or 7, characterized in that the reaction of the unsaturated carboxylic acid with the activated polymer is carried out in the presence of an organic solvent for the polymer or graft copolymer, respectively.

9. Process for producing graft copolymers substantially as hereinbefore described with reference to the examples.

10. Shaped articles and especially films and other structures having one dimension much smaller than the other two substantially as hereinbefore described with reference to the examples.

11. Graft copolymers of a polyolefin backbone material and an unsaturated carboxylic acid grafted thereon whenever prepared by the process claimed in claim 9.

BOULT, WADE & TENNANT,

111 & 112, Hatton Garden, London, E.C.1.
Chartered Patent Agents.